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(54) **Biologically active glass**

(57) A biologically active glass and glass-ceramic composition useful for making surgical and dental implants comprising, by mol%,:

SiO_2	35 ~ 60
B_2O_3	5 ~ 15
Na_2O	10 ~ 30
CaO	5 ~ 40
TiO_2	0.5 ~ 10
P_2O_5	0 ~ 15
K_2O	0 ~ 20
Li_2O	0 ~ 10
MgO	0 ~ 5
$Al_2O_3 + ZrO_2 + NB_2O_5$	0 ~ 8
$La_2O_3 + Ta_2O_5 + Y_2O_3$	0 ~ 8
F_2	0 ~ 15.

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FIG. 1

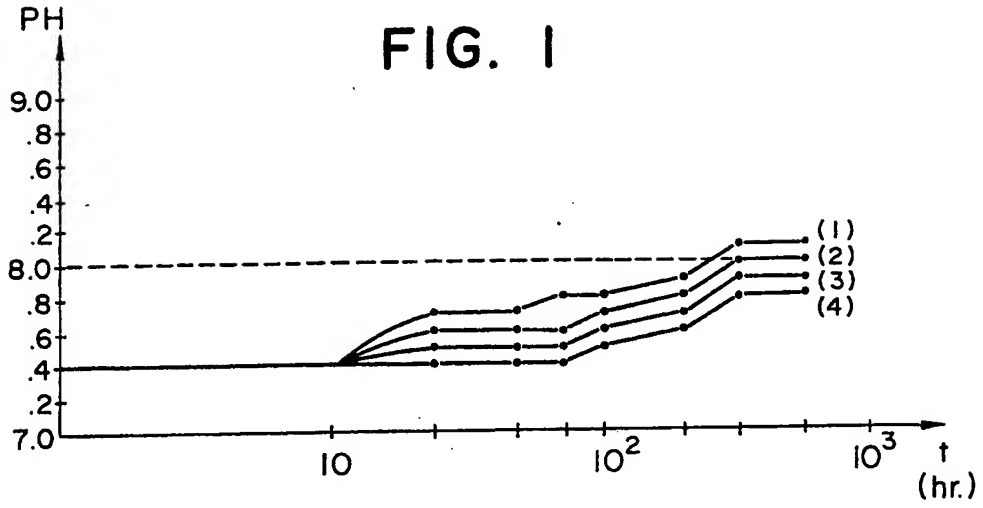


FIG. 2

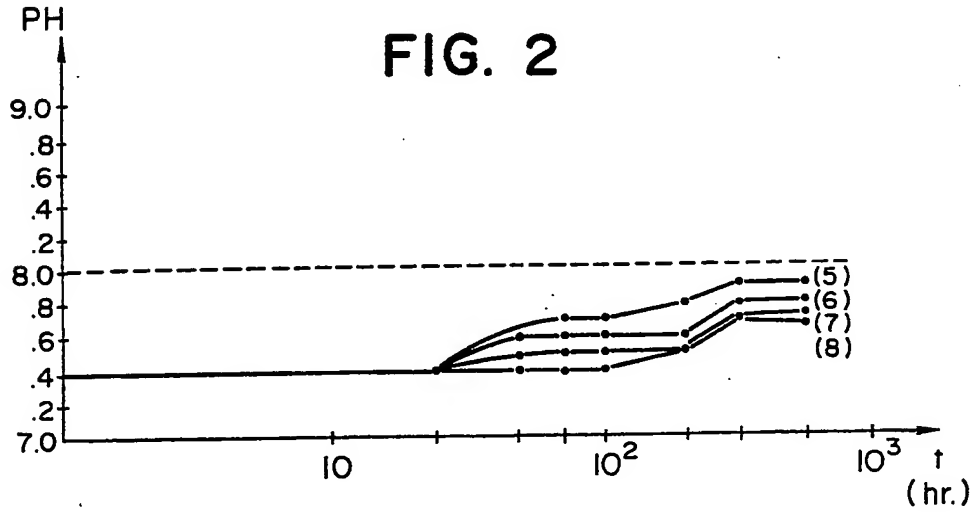
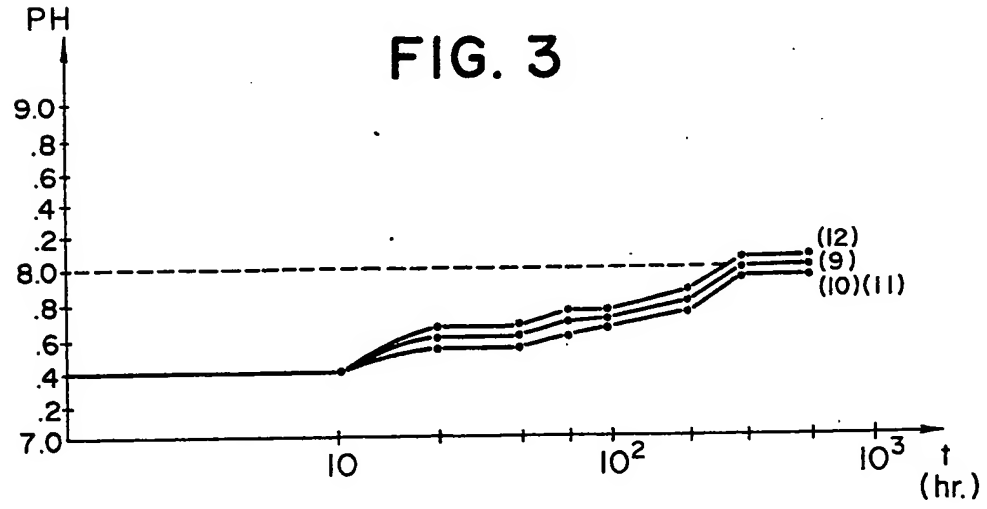


FIG. 3



SPECIFICATION

Biologically active glass and glass ceramics

The present invention relates to a biologically active glass and glass-ceramic composition and an implant coated with the composition.

In the art there are known biologically active glass and glass ceramics which are able chemically to combine directly with hard tissues, in particular, bones in a living body. Upon contacting the body fluids in vivo, the biologically active material reacts and bonds to bones. The mechanism of the reaction between the material and the hard tissue in a living body is described in detail in a publication, J. Biomed. Mater. Res. Symp. No. 2 (Part 1), 117-141 (1971). In summary, the mechanism is as follows:

Constituents of the material such as Na, Ca, P, B and Si are dissolved out from the surface of the material into the body fluid as the respective ions thereby forming micro pores on the surface. P and Ca ions derived from the biologically active material and also P and Ca ions derived from the living body itself owing to its bone making ability are gradually deposited in the formed pores and crystallized into hydroxylapatite which is the main substance of bone. Thus, a direct and chemical bonding is obtained between the biologically active material and the bone.

On the other hand, it is known that no practically useful implant can be produced using only such a biologically active material because of its insufficient mechanical strength. For a solution to the problem, the employment of a metal core having a high mechanical strength sufficient to resist the load normally applied thereto in use, with a coating of such biologically active glass or glass ceramics, has been proposed, and clinical tests have been made for implants thus fabricated.

To apply the coating of biologically active material to the metal core there have been used various methods in which the biologically active glass and glass ceramics have to be molten as a rule. In this case, a preferred coating process is an enamelling process which enables a uniform coating to be realized. However, use of the enamelling process is allowed only when the biologically active material and the metal core to be coated with the material have nearly equal coefficients of thermal expansion and the biologically active material has a relatively low melting point. If the biologically active material and the metal core have different coefficients of thermal expansion, then cracks will easily be developed in the coating layer after cooling. Also, if the biologically active material is not fusible at relatively low temperatures, then the high temperature molten glass or glass ceramics may damage the core and furthermore, the coating may be contaminated with metal ions.

From the above it is concluded that biologically active glass and glass ceramics to be applied to a metal core to form an implant are required to satisfy the following requirements all at once:

1) To have an adequate reactivity to allow leaching of various ions from its surface;

2) To have a coefficient of thermal expansion substantially equal to that of the metal core and

3) To have a relatively low melting point.

All of the known biologically active glass and glass ceramics can not satisfy the above requirements all at once. For example, mention may be made of those biologically active glass and glass ceramics as disclosed in Japanese Patent Application Laid Open No. 145,394/1978 the counterparts of which are U.S. Patent Nos. 4,159,358 and 4,234,972. Within the range of ingredient contents allowable for composing the biologically active material specified therein, it is not possible to obtain many combinations of the reactivity and coefficient of thermal expansion. In more detail, if the composition of the biologically active material is selected in such manner as to give the material a coefficient of thermal expansion substantially equal to that of the metal core to be coated with the material, then the reactivity of the material is determined thereby. It is no longer possible to determine the reactivity independently of the selected coefficient of thermal expansion.

When one wishes to form an implant by coating a metal core with any known biologically active material, the coefficient of thermal expansion of the coating material must first be determined, considering the coefficient of thermal expansion of the core. Since, as noted above, the reactivity of the material is determined by the selected coefficient of thermal expansion, there is left almost no possibility of free selection of the reactivity after the selection of coefficient of thermal expansion for biologically active glass and glass ceramics hitherto known. However, selection of reactivity is of great importance for usefulness of a biologically active implant as will be seen from the following description.

We, the inventors of the present invention, have conducted a number of experiments on the biologically active glass and glass ceramics proposed by the prior invention, that is, the aforementioned Japanese Patent Application Laid Open No. 145,394/1978 to examine the strength of chemical bonding between the material and various bones. In these experiments in vivo, the known biologically active materials were implanted in thighbones of rats, craniums of rabbits and jawbones of dogs. The results obtained from these animal experiments demonstrated the fact that the chemical bonding strength between the biologically active material and bones is variable according to the kind of test animal and also, even in the same kind of animal, according to age, and condition of the animal and also the position where implantation was made. This difference in the bonding strength obviously resulted from the difference in bone forming ability between different living bodies and also between different parts of the body.

As previously described, when the biologically active material is implanted in a living body, the reaction takes place on the surface of the material a chemical reaction by which ions are leached from the surface and thereby micro pores are formed on the surface. With the proceeding of the surface reaction, new bone is formed owing to the bone forming ability of the living body and the micro pores in the material

are gradually filled up with th new bone. A perf ct and str ng biologically activ material-to-bone bond can be attained only when th surface reaction proceeds at a speed substantially qual to th bone making speed. Th refore, in case that the reactivity of the used biologically active material can not follow the bone forming ability of the body part where the material was implanted, it will result in poor bonding strength.

Accordingly, for clinical use of an implant having a coating of biologically active glass or glass ceramics, it is essential to employ such biologically active material, the reactivity of which corresponds to the bone forming ability of the body part where the implant is to be implanted.

As a result of the aforementioned surface reaction of the biologically active material in vivo, ions such as Na, Ca, P, B and Si are leached from the surface. The amount of leaching ions is predominant in Na and Ca. Leaching of other ions such as P, B and Si is gradual and begins after the glass structure has been destroyed to some extent as a result of leaching of Na and Ca ions. This means that evaluation of the reactivity of a biologically active material to a living body can be conducted simply by observing the change of pH primarily attributable to the leached Na ion. More particularly, the material is brought into a simulated physiological solution particularly prepared for this purpose and it is held immersed in the solution long enough to observe the change in pH of the solution resulting mainly from the leaching of Na ion from the material in the solution. In this manner, the evaluation of reactivity of the material to a living body can be performed by a simple pH test in vivo.

Accordingly, it is an object of the invention to provide biologically active glass and glass ceramics with which one can select at will any desirable combination of coefficient of thermal expansion and reactivity regarding the reaction by which ions are leached from the surface of the material when contacted with body fluids in a living body, and also which have a relatively low melting point.

It is another object of the invention to provide improved metal implants covered with a coating of such biologically active glass or glass ceramics.

To attain the above objects according to the present invention there is provided a biologically active glass and glass-ceramic composition essentially comprising, by mol %,:

SiO_2	35 ~ 60
B_2O_3	5 ~ 15
Na_2O	10 ~ 30
CaO	5 ~ 40
TiO_2	0.5 ~ 10
P_2O_5	0 ~ 15
K_2O	0 ~ 20
Li_2O	0 ~ 10
MgO	0 ~ 5
$Al_2O_3 + ZrO_2 + Nb_2O_5$	0 ~ 8
$La_2O_3 + Ta_2O_5 + Y_2O_3$	0 ~ 8
F_2	0 ~ 15

Also, th re is provided an implant cov red with a coating of th abov defin d biologically active material.

Th r has thus b en outlin d rather broadly th more important features of the inv ntion in rd r that the detailed description th reof that follows may be better understood and in order that the present contribution to th art may be better appreciated. There are, of course, additional features of the invention that will be described hereinafter and which will form the subject of the claims appended hereto. Those skilled in the art will appreciate that the conception upon which this disclosure is based may readily be utilized as a basis for the designing of other structures for carrying out the several purposes of the invention. It is important, therefore, that the claims be regarded as including such equivalent constructions as do not depart from the spirit and scope of the invention.

Specific embodiments of the invention have been chosen for purposes of illustration and description, and are shown in the accompanying drawings, forming a part of the specification wherein:

Fig. 1 is a graph showing the change of pH with time for a first group of embodiments of the composition according to the invention shown in Table 1;

Fig. 2 is a similar graph for a second group of embodiments shown in Table 2; and

Fig. 3 is a similar graph for a third group of embodiments shown in Table 3.

We have found that the reactivity of known biologically active glass and glass ceramics can be controlled very effectively by adding TiO_2 to the known composition even in a very small amount. Based upon the finding, we have found a novel composition of biologically active glass and glass ceramics useful for coating a metal core with the same to form implants. The novel composition has successfully broadened the selection range of reactivity for biologically active glass and glass ceramics.

For biologically active glass and glass ceramics hitherto proposed, a high content of B_2O_3 was required to attain the characteristic of low melting point. This resulted in an excess of reactivity so that any strong bonding between the biologically active material and bones could not be attained. In contrast, according to the invention, one can obtain biologically active glass and glass ceramics having the reactivity adjusted to a suitable level using TiO_2 even when a large amount of B_2O_3 must be contained in the biologically active material to satisify the requirement of low melting point.

Biologically active glass and glass ceramics according to the invention are essentially composed of:

SiO_2	35 ~ 60	(by mol %)
B_2O_3	5 ~ 15	
Na_2O	10 ~ 30	
CaO	5 ~ 40	
TiO_2	0.5 ~ 10	
P_2O_5	0 ~ 15	
K_2O	0 ~ 20	
Li_2O	0 ~ 10	
MgO	0 ~ 5	
$Al_2O_3 + ZrO_2 + Nb_2O_5$	0 ~ 8	
$La_2O_3 + Ta_2O_5 + Y_2O_3$	0 ~ 8	and
F_2	0 ~ 15	

The biologically active material according to th invention includes all of th glass and glass-c ramics defin d ab ve. For th above composition it is unn c ssary t differentiat glass fr m glass ceramics. As well known to those skilled in the art, glass can be crystallized into ceramics for the purpose of increasing its strength.

The above specified contents of the respective ingredients in the composition according to the invention are essential for the following reasons:

As mentioned above, TiO_2 is an essential ingredient to reduce the reactivity of the biologically active material. With a content above 10 mol % of TiO_2 the biologically active material can not have the desired characteristic of low melting point. Below 0.5 mol %, the reaction reducing effect of TiO_2 is too small to adjust the reactivity of the material to the desired level.

B_2O_3, Na_2O and CaO have some effect on the reactivity although the effect is far smaller than that of TiO_2. The reactivity increases with increase of the content of these ingredients. Therefore, in case that the content of these ingredients is extremely high or extremely low, then it is impossible to adjust the reactivity to the desired level. For that reason, the content of B_2O_3 should be in the range of from 5 to 15 mol %. Similarly, the content of Na_2O should be within the range of 10 to 30 mol % and that of CaO be within the range of 5 to 40 mol %.

SiO_2 is a network former. The reactivity of the biologically active material increases with decrease of the content of SiO_2. However, its effect on the reactivity is remarkably smaller than that of TiO_2. With a higher content of SiO_2 than 60 mol %, the material can not have the desired characteristic of low melting point. Below 35 mol % of SiO_2, it is impossible to adjust the reactivity of the material to the desired level even when it is controlled by TiO_2.

K_2O and Li_2O may be used in place of Na_2O to control the reactivity and also to render the material fusible at relatively low temperatures. Above 10 mol % of Li_2O, the biologically active material loses its affinity for a living body.

MgO is substitutive for CaO. Above 5 mol % MgO, the composition loses its affinity for a living body.

A_2O_3, ZrO and Nb_2O_3 are substitutive for TiO. However, the content of these ingredients in total should be less than 8 mol %. Above 8 mol %, the biologically active material can not have the desired characteristic of low melting point.

F_2 serves to make the material fusible at relatively low temperatures. Above 15 mol % of F_2, it is impossible to give the composition an adequate reactivity.

A higher content than 8 mol % of La_2O_3, Ta_2O_5 and Y_2O_3 in total makes it impossible to render the material fusible at relatively low temperatures.

Above 15 m l % of P_2O_5, th material can not have any suitabl reacitivity.

Within the sc p of th composition defined above, such glass and glass ceramics are particularly suitabl for coating a metal core employing the enam lling pr cess which are comp s d of:

SiO_2	40 ~ 60	m l %
B_2O_3	8 ~ 15	
Na_2O	15 ~ 30	
CaO	8 ~ 30	
TiO_2	0.5 ~ 8	
P_2O_5	0 ~ 8	and
F_2	0 ~ 15.	

Because of high content of B_2O_3, this group of glass and glass ceramics are fusible at temperatures low enough to apply the biologically active coating to a metal core by enamelling. In addition, because of a high content of Na_2O, the coating layer of this composition is tightly bonded to the core metal.

In contrast, biologically active glass and glass ceramics hitherto known have generally a high melting point even in the form of powder. Therefore, they are unsuitable for the enamelling process. When a coating of the known material is applied to a metal core, a large amount of metal ions are diffused into the glass so that the function of the coating as a biologically active material may be lost to a great extent.

The following examples illustrate the effect of the present invention.

Examples 1-4

Four different samples of glass and glass ceramics according to the invention were prepared as shown in Table 1. As for the contents of B_2O_3, SiO_2, Na_2O and CaO, the four samples, Examples 1 to 4 were equal or approximately eqaul to each other. However, the content of TiO_2 was varied from sample to sample between 0.5 mol % and 3.0 mol %. The content of B_2O_3 in these examples is higher than that of the prior art biologically active glass and glass ceramics.

Measurements were conducted on the samples of Examples 1-4 to determine the coefficient of thermal expansion and the melting point in the form of powder. Values found are also given in Table 1.

Table 1

Example No.	(1)	(2)	(3)	(mol %) (4)
SiO_2	49.5	49.0	48.5	48.5
B_2O_3	12.0	12.0	12.0	11.0
Na_2O	23.0	23.0	22.5	22.5
CaO	15.0	15.0	15.0	15.0
TiO_2	0.5	1.0	2.0	3.0
Coefficient of thermal expansion (10^{-7} °C^{-1})	130	130	130	130
Melting point as powder (°C)	690	690	690	695

As seen in Table 1, the biologically active glass and glass caeramics exhibited the same coefficient of thermal expansion. Their melting points as powd r were v ry low which were 690°C and the vicinity of 690°C. Furthermor , as seen in Fig. 1, the reactivity f th biologically activ mat rial was successfully changed by changing th content f TiO_2.

Fig. 1 sh ws changes f pH f a simulated physi logical solution with time for abov Examples 1-4 sh wn in Table 1. Curves (1), (2), (3) and (4) were obtain d from the compositions of Examples 1, 2, 3 and 4 respectively in the following procedure:

Each sampl was imm rsed in a simulated physiol gical solution and h ld immersed for a long time during which pH of the solution was continuously m asured. Found values of pH were then plotted as shown in Fig. 1 with the pH of th solution as the ordinate and the treating time (hr.) in logarithmic notation as the abscissa.

Fig. 1 indicates that the highest value of pH was obtained for the composition of Example 1 in which the content of TiO_2 was the smallest of all the four compositions and that the lowest pH was for the composition of Example 4 having the largest content of TiO_2 of all. This demonstrates that the reactivity of the biologically active material according to the invention can be controlled effectively by changing the content of TiO_2. The degree of increase of pH becomes smaller as the content of TiO_2 is increased and therefore it is obvious that the reactivity of the material to a living body can be reduced by increasing the content of TiO_2.

The biologically active glass of Example 1 which exhibited the highest reactivity in the above pH test was shaped into a cylinder of 1 mm in diameter x 3 mm in length. The cylinder was implanted in a thighbone of a rat where the level of bone forming ability is relatively high. On the other hand, the biologically active glass of Example 3, the reactivity of which was found to be relatively low, was shaped into a cylinder of 3 mm in diameter x 5 mm in length. The cylind r was implanted in th jawbone of a dog where th lev l of bone forming ability is relatively low. In both of the two experim nts in vivo, there was obtain d a strong glass-to-bone bond.

For the purpose of comparison, a known biological active material disclosed in the above referred to patent publication, Japanese Patent Application Laid Open No. 145,394/1978 and named "Bioglass A" was tested in the same manner as above. Although the known material exhibited a high bonding strength t the thighbone of rat, the bonding obtained between the material and the jawbone of dog was poor in strength.

Biologically active materials known from the above referred to patent publication have high melting points as powder which were measured to be about 1100°C or higher. This is far higher than that of the materials according to the present invention. It is possible to lower the high melting point to some extent by adding B_2O_3 to the known composition. However, addition of B_2O_3 more than 10 mol % causes the known composition to have an excess reactivity. In this case, unlike the material according to the invention, it is very difficult to adjust the reactivity to a desired level.

Examples 5-8

Further examples are shown in Table 2 as Examples 5-8.

Table 2

Example No.	(5)	(6)	(7)	(8) (mol %)
SiO_2	48.0	47.5	47.0	47.0
B_2O_3	12.0	12.0	12.0	11.5
Na_2O	23.0	23.0	23.0	23.0
CaO	12.5	12.5	12.5	12.5
CaF_2	2.0	2.0	2.0	2.0
AlF_3	2.0	2.0	2.0	2.0
TiO_2	0.5	1.0	1.5	2.0
Coefficient of thermal expansion (10^{-7} °C^{-1})	135	135	135	135
Melting point as powder (°C)	670	670	670	675

This group of biologically active compositions shown in Table 2 contains fluorides in addition to the ingredients shown in Table 1. Fluorides serve to reduce the reactivity of the biologically active composition as a whole as seen in Fig. 2 showing the change of pH with time similarly to Fig. 1. The reduced reactivity is further adjusted to a desired level by changing the content of TiO_2 (See Fig. 2). These compositions have the same coefficient of th rmal xpansion, which makes it convenient to coat th same kind f m tal cores with different biol gically activ compositions. The m lting points of this group f biol gically activ compositions in th form of powd r are all low which are about 670°C.

Examples 9-12

Still further examples of preferred biologically activ glass and glass-ceramic compositions are shown in Table 3 as Examples 9-12.

This group of compositions contain some further ingredients in addition to the ingredients shown in Table 2.

K_2O and Li_2O may be added in place of Na_2O to attain the same effect. Al_2O_3, ZrO_2 and Nb_2O_5 have the effect of controlling the reactivity of biologically active material and therefore may be used to assist TiO_2 in controlling the reactivity. Addition of La_2O_3, Ta_2O_5 and Y_2O_3, even in a very small amount, produces such biologically active glass and glass ceramics which xhibit a high X-ray absorpti n coeffici nt which makes it easy to observe the implant after implanati n. Addition of P_2O_5 has the effect of improving th affinity f the material to a living body. MgO has a similar function to CaO and therefore it is substitutiv for CaO.

Table 3

Example No.	(9)	(10)	(11)	(mol %) (12)
SiO_2	48.0	48.0	47.5	46.0
B_2O_3	12.0	12.0	12.0	11.0
Na_2O	21.5	6.5	21.0	20.0
CaO	15.0	10.0	15.0	13.5
TiO_2	1.0	1.0	0.5	1.0
P_2O_5	2.5	2.5	2.5	2.5
K_2O	–	10.0	–	–
Li_2O	–	5.0	–	–
A_2O_3	–	–	0.5	–
ZrO_2	–	–	0.5	–
Nb_2O_5	–	–	0.5	–
La_2O_3	–	–	–	2.0
Ta_2O_5	–	–	–	2.0
Y_2O_3	–	–	–	2.0
MgO	–	5.0	–	–
Coefficient of thermal expansion (10^{-7} °C^{-1})	130	120	130	135
Melting point as powder (°C)	690	690	700	740

This group of compositions shown in Table 3 also has the desired characteristic of low melting point. Further, as seen in Fig. 3, all of the compositions showed the desired level of reactivity. The reactivity can be further finely controlled by changing minutely the contents of TiO_2, A_2O_3, ZrO_2 and Nb_2O_5 serving as reaction controller.

The glass and glass ceramics according to the invention can be applied to a metal core to form an implant. The metal core to be covered with a coating of the biologically active material may be made of any suitable metal such as stainless steel, cobalt-chromium alloy, titanium, titanium alloy, noble metals, for example, platinum, noble metal alloy, for example, plantinum (90%) – rhodium (10%) alloy or molybdenum-nickel-cobalt-chromium alloy. Preferably the coating layer is 0.1 to 2 mm thick. Coating may be carried out employing a suitable known coating process such as enamelling and sealing.

Therefore, the present invention includes also such metal implants coated with the above defined glass and glass ceramics. The following examples, Example 13 is given to illustrate the implant according to the invention.

Example 13

A cylindrical metal core of 5 mm in diameter and 10 mm in length was formed of an alloy comprising:

Ni	59 wt. %
Cr	15
Co	15
M	7 and
oth rs	4.

The cylindrical m tal core was then subjected to a sandblast tr atment by alumina particles of 180 grit under th pressure of 8 kg/cm^2. This surface treatment is us ful for reinforcing th bonding strength of glass-to-metal chemical bond by th aid f mechanical bond.

Following the surface treatment, the core was subjected to a supersonic cleaning in acetone for three minutes. The metal core was then held in vacuum over 10^{-6} Torr at 800°C for a half hour for degassing. This degassing has the effect of preventing bubbling from the surface of the core when it is brought into contact with molten glass of high temperature.

The glass composition of Example 1 described above was milled into powder whose particle size was less than 200 mesh. The powdered glass was then mixed with the same volume of a solvent mixture such as 10:1 by volume mixture of ethanol and triethanolamine to form a slurry. The slurry was applied to the pretreated metal core by dipping or coating to produce a slurry layer about 3 mm thick on the metal core with its one end surface being left uncoated.

The metal core carrying the layer of slurry coating was placed within a heating furnace. The temperature in the furnace was raised from room temperature to 680°C in a half hour and held at 680°C for three minutes. During this period of heating, organic materials contained in the slurry layer were all vaporized or burnt off and the molten fine glass particles bonded together so as to form a glass coating layer covering the metal core. The coated metal core was then transferred into another heating furnace being held at 450°C. After leaving the coated metal core standing in the furnace for five hours or more, it was cooled to the room temperature. Thus, an implant comprising a metal core and a coating layer of biologically active glass was prepared.

If desired, the implant thus prepared may be further treated by holding it at a temperature ranging from 600 to 700°C for about an h ur t cause a phase s paration r a crystal phase formation in the glass coating layer.

As understo d from th f regoing, the present inv ntion brings forth various advantages v r th prior art.

According to the invention, any desired combination of reactivity and thermal expansion coefficient may be selected for bioligically active glass and glass ceramics by suitably selecting the content of TiO_2. Therefore, the present invention permits the preparation of many biologically active materials having different reactivity levels for a kind of metal core. Thus, by coating metal cores made of the same kind of metal with differently reactive biologically active materials there can be provided various implants having different reactivities. The operator, therefore, can select a most suitable implant for a patient who undergoes an implanting operation while considering the bone forming ability determined by the age and condition of the patient as well as the position at which the implant is to be located. This always assures a better solution than does the prior art.

Another advantage of the biologically active materials according to the invention resides in lower melting point. Owing to the characteristic of low melting point, the coating material can be applied to a metal core employing the preferred enamelling process which provides a high quality and uniform coating at a higher work efficiency. Since a uniform coating can be obtained, work on the implant after coating can be done very easily.

Implants coated with the glass and glass ceramics according to the invention are tightly bonded to bones. Therefore, they are useful, for example, as a substitute material for bone, bone reinforcing material and dental roots. It is evident that the present invention makes a great contribution to medicine.

We believe that the preparation and use of our biologically active glass and glass ceramics composition will now be understood and that the several advantages thereof will be fully appreciated by those persons skilled in the art.

CLAIMS

1. A biologically active glass and glass-ceramic composition comprising essentially, by mol %,:

SiO_2	35 ~ 60
B_2O_3	5 ~ 15
Na_2O	10 ~ 30
CaO	5 ~ 40
TiO_2	0.5 ~ 10
P_2O_5	0 ~ 15
K_2O	0 ~ 20
Li_2O	0 ~ 10
MgO	0 ~ 5
$Al_2O_3 + ZrO_2 + Nb_2O_5$	0 ~ 8
$La_2O_3 + Ta_2O_5 + Y_2O_3$	0 ~ 8 and
F_2	0 ~ 15.

2. A biologically active glass and glass-ceramic composition as set forth in Claim 1, which comprises essentially, by mol %,:

SiO_2	40 ~ 60
B_2O_3	8 ~ 15
Na_2O	15 ~ 30
CaO	8 ~ 30
TiO_2	0.5 ~ 8
P_2O_5	0 ~ 8 and
F_2	0 ~ 15.

3. An implant coated with a layer of a biologically active glass and glass-ceramic composition comprising essentially, by mol %,:

SiO_2	35 ~ 60
B_2O_3	5 ~ 15
Na_2O	10 ~ 30
CaO	5 ~ 40
TiO_2	0.5 ~ 10
P_2O_5	0 ~ 15
K_2O	0 ~ 20
Li_2O	0 ~ 10
MgO	0 ~ 5
$Al_2O_3 + ZrO_2 + Nb_2O_5$	0 ~ 8
$La_2O_3 + Ta_2O_5 + Y_2O_3$	0 ~ 8 and
F_2	0 ~ 15.

4. An implant as set forth in Claim 3 wherein said coating layer of biologically active composition is 0.1 to 2 mm thick.

5. A biologically active glass according to claim 1 substantially as herein described with reference to any one of the Examples.

6. An implant according to claim 3 substantially as herein described with reference to Example 13.

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